

In situ generation of diazonium cations in organic electrolyte for electrochemical modification of electrode surface

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ABSTRACT

The modification of glassy carbon electrode was achieved by electrochemical reduction of *in situ* generated diazonium cations in acetonitrile. The *in situ* generation of 4-nitrophenyl diazonium cations in acetonitrile was investigated by spectroscopic methods. UV–visible spectroscopy revealed slow kinetics for the reaction of 4-nitroaniline with *tert*-butylnitrite in acetonitrile to form the corresponding diazonium cation. As a result, a coupling reaction, which implies a consumption of the amine and loss of the already formed diazonium cations, was evidenced by ^1H NMR spectroscopy. This spectroscopic study allowed the optimization of the *in situ* diazonium cations generation prior to the modification step. The electrochemical modification of the carbon electrodes with 4-nitrophenyl, 4-bromophenyl and anthraquinone groups was characterized by cyclic voltammetry and the resulting grafted layer were characterized by electrochemical techniques. The cyclic voltammetric behaviour during the electrochemical grafting was very similar to the one observed for an isolated diazonium salt dissolved in acetonitrile. In the case of the anthraquinone-modified electrode, the use of acetonitrile, into which the corresponding amine is soluble but not in aqueous media, allowed for its grafting by the *in situ* approach. The barrier properties of these grafted layers are similar to those obtained from isolated diazonium salts. Finally, the chemical composition of the grafted layers was determined by X-ray photoelectron spectroscopy and surface coverage in the range $5\text{--}7 \times 10^{-10} \text{ mol cm}^{-2}$ was estimated for films grown in our experimental conditions.

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1. Introduction

Carbon surface modification, either by chemical or electrochemical reduction of diazonium cations is an attractive way to confer new functions to this material. This derivatization method, which was first introduced by Pinson and coworkers [1,2], has been widely investigated during the past decade [3–7]. It consists in the reduction of an aryl diazonium cation to the corresponding aryl radical which can further react with a carbon substrate surface atom to yield the covalent bonding of this aryl group (Scheme 1).

This modification procedure is very attractive because it avoids the use of oxidative conditions which can lead to the detrimental oxidation of the carbon substrate [8,9] and also because it allows the presence of selected functional groups on the aryl groups. On the other hand, a major disadvantage of the modification approach based on aryl diazonium salt is that the synthesis of the salt is required. Indeed, the synthesis and isolation of the diazonium salt are not always straightforward. The synthesis is commonly carried out in acidic media from the corresponding amine by using NaNO_2

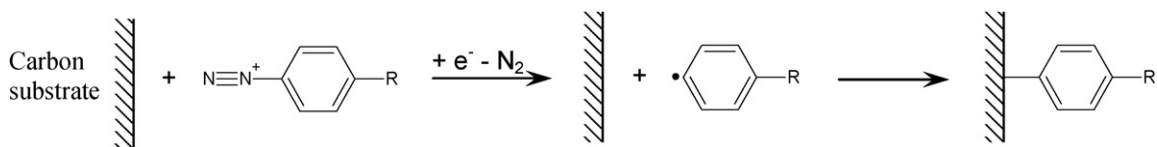
as a reactant [3,10–12]. This synthesis is followed by a separation and purification step. A simpler procedure was already described by Morita et al. [13], Blankespoor et al. [14], Corgier et al. [15,16] and very recently our group [17,18] reported that an aromatic amine can be transformed into a diazonium by a standard diazotization procedure [19] and that the resulting solution can be used to modify carbon [13–16,18] or gold [17] electrodes by electrochemical reduction. However, those studies only described the grafting from an aqueous medium, which limits the surface modification to water-soluble and non-hydrolysable molecules.

In this work, we report the *in situ* generation of diazonium cations in acetonitrile. The synthesis of diazonium cations is carried out by the reaction of an amine with *tert*-butylnitrite to form the corresponding diazonium cation following a reaction previously described by Doyle and Bryker [20]. This reaction is described in Scheme 2.

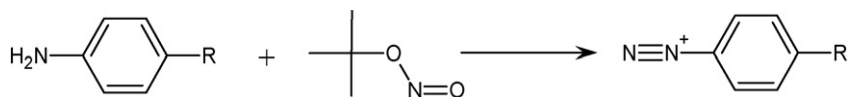
In situ generated cations were then electrochemically reduced to obtain a grafted layer on glassy carbon electrodes. To validate this method for surface modification, it was applied to three diazonium cations: 4-nitrophenyl diazonium, 4-bromophenyl diazonium and anthraquinone-1-diazonium. The grafting of anthraquinone molecules is of particular interest because the corresponding amine is not soluble in aqueous media.

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Scheme 1. Electrochemical reduction of diazonium cations and grafting step.



Scheme 2. Diazotization of an amine with *tert*-butylnitrite.

2. Experimental

The diazonium cations used for the derivatization of the glassy carbon electrode were identified as follows: 4-bromophenyl diazonium (Br-PD), 4-nitrophenyl diazonium (NO₂-PD) and anthraquinone-1-diazonium (AQ-D).

2.1. Reagents

Tetraethylammonium tetrafluoroborate (NEt₄BF₄) (Aldrich) was dried by heating at 80 °C under vacuum for 24 h. Potassium ferricyanide, potassium ferrocyanide, potassium chloride, sodium hydroxide, para-substituted anilines used for diazonium salt synthesis, *tert*-butylnitrite and 4-nitrophenyl diazonium tetrafluoroborate were used as received from Aldrich.

2.2. Electrode preparation and modification

Working electrodes made of glassy carbon were obtained from Bioanalytical Systems Inc. (Model MF-2012; diameter 3 mm). Platinum gauze of ca. 1 cm² was used as counter electrode. All potentials were reported versus the reference electrode Ag/AgCl (saturated KCl). The glassy carbon electrode surface was cleaned by polishing with Buehler 1 and 0.05 μm alumina slurry (Tech-Met Canada). After each polishing the electrode was washed with Nanopure water (18.2 MΩ cm) by sonication and kept in water. Prior to the electrochemical derivatization, the electrode was sonicated in acetonitrile.

The diazonium cations (NO₂-PD, Br-PD or AQ-D) were synthesized by adding 1 mM of the corresponding amine to a solution containing 3 mM of *tert*-butylnitrite and 0.1 M (Et)₄NBF₄ as supporting electrolyte in acetonitrile. The electrolytic solution was left to react for 10 min. The solution used to form a grafted layer on the glassy carbon electrode after 10 min of reaction is composed of 1 mM of diazonium cations, 2 mM of *tert*-butylnitrite and 0.1 M (Et)₄NBF₄.

The solution containing the electroactive probe was ferricyanide/ferrocyanide (5 mM; 0.1 M KCl, adjusted at pH 7 with a 1 M KOH solution). All solutions were deaerated with extra dry nitrogen during 15 min. The relative electroactivity of the modified electrode, which is inversely related to its blocking properties, was quantified by cyclic voltammetry in the presence of ferricyanide/ferrocyanide. The parameter I_{rel} is defined as:

$$I_{rel} (\%) = \frac{\text{anodic peak current with a film}}{\text{anodic peak current for a bare electrode}} \times 100 \quad (1)$$

The strong dependence of I_{rel} to the experimental procedure and electrode parameters (electron transfer rate, surface coverage and physicochemical properties [18], potential range), limits its accuracy for quantitative surface coverage determination. However, this parameter is strongly correlated with the charge transfer resistance

measured by electrochemical impedance spectroscopy [18]. Thus, the I_{rel} parameter can give a good qualitative description of the electrode surface coverage.

The surface concentration, Γ_{AQ} , of the grafted anthraquinone (AQ) groups is computed from:

$$\Gamma_{AQ} = \frac{Q}{nFS} \quad (2)$$

where Q is the charge of anodic or cathodic peak, n the number of electrons exchanged per reactant molecule ($n=2$), F is the Faraday constant (96,487 C mol⁻¹) and S is the geometric surface of the electrode ($S=0.07$ cm²).

2.3. Instrumentation and procedure

NMR measurements were performed with a Gemini 300 MHz spectrometer (Varian Instruments) in deuterated acetonitrile.

Electrochemical measurements were performed in a one-compartment cell using a three-electrode configuration. Cyclic voltammetry and chronoamperometry were carried out using either a potentiostat or galvanostat electrochemical interface SI1480 (Solartron Instruments) interfaced with a PC, and the electrochemical setups were controlled with DC Corrware (Scribner Associates, version 2.8d) software.

X-ray photoelectron spectra (XPS) were obtained on glassy carbon plates (GLCP-10; The Electrosynthesis Co.) with a VG Escalab 220i-XL equipped with a hemispherical analyzer and an Al anode (Kα X-rays at 1486.6 eV) used at 12–14 kV and 10–20 mA. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below 10⁻⁹ Torr. XPS survey spectra were recorded with a pass energy of 100 eV and an energy increment of 1 eV whereas the pass energy was 20 eV and the energy increment was 100 meV for the core level spectra. Core level spectra were used to evaluate the atomic concentrations of the species present at the glassy carbon electrode surface. The atomic concentrations (at.%) of each individual element were determined from the relative peak areas of the spectra and the corresponding sensitivity factors according to:

$$\text{at.}\% = \frac{A_i/s_i}{\sum_i A_i/s_i} \quad (3)$$

where A_i is the peak area of the element i and s_i is the sensitivity factor for this element. For example, values of 1, 1.8, 2.93 and 2.84 were used for C1s, N1s, O1s and Br3d, respectively.

3. Results and discussion

3.1. Spectroscopic characterization of diazonium cations synthesis

Optimization of the parameters for the NO₂-PD synthesis by reaction of nitroaniline with *tert*-butylnitrite in acetonitrile was

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